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Synthesis of cerium oxide nanoparticles using *Gloriosa superba* L. leaf extract and their structural, optical and antibacterial properties

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ABSTRACT

CeO_2 nanoparticles (NPs) were green synthesized using *Gloriosa superba* L. leaf extract. The synthesized nanoparticles retained the cubic structure, which was confirmed by X-ray diffraction studies. The oxidation states of the elements (C (1s), O (1s) and Ce (3d)) were confirmed by XPS studies. TEM images showed that the NPs possessed spherical shape and particle size of 5 nm. The Ce–O stretching bands were observed at 451 cm^{-1} and 457 cm^{-1} from the FT-IR and Raman spectra respectively. The band gap of the CeO_2 NPs was estimated as 3.78 eV from the UV–visible spectrum. From the photoluminescence measurements, the broad emission composed of eight different bands were found. The antibacterial studies performed against a set of bacterial strains showed that Gram positive (G+) bacteria were relatively more susceptible to the NPs than Gram negative (G−) bacteria. The toxicological behavior of CeO_2 NPs was found due to the synthesized NPs with uneven ridges and oxygen defects in CeO_2 NPs.

1. Introduction

Phytosynthesis of metal and metal oxide nanoparticles (NPs) is an emerging field of nanoscience and technology. Size, shape conjointly plays a vital role in physical, chemical, electrical and optical properties of nanomaterials. Cerium oxide (CeO_2) is a semiconductor with wide band gap energy (3.19 eV) and large exciton binding energy. It is used in wide range of applications such as, catalyst, sensor, solid oxide fuel cells, sun screen cosmetics, bioimaging, biotransformation and antibacterial activity [1–7]. Generally, CeO_2 NPs were synthesized by physical and chemical methods such as hydrothermal, flame spray pyrolysis, sonochemical, microwave, sol–gel, and co-precipitation [8–13]. However, most of the techniques are complex, time consuming, expensive and hazardous [14–23] (Table. 1). The green chemistry approaches to the development in phytosynthesis of metal and metal oxide NPs. This method offers a plenty of advantages such as cost-effectiveness, large-scale commercial production and pharmaceutical applications. The CeO_2 NPs was less toxic when compared to TiO_2 and ZnO NPs in cell line activity [24]. Recently, the CeO_2 NPs have been synthesized using honey, egg white and fungal extracellular compounds [18,25,26]. These biocomponents which act as capping and reducing agent render to produce a nanocrystalline nature of metal oxide NPs in different sizes and morphology. In this paper, the synthesis of CeO_2 NPs using *Gloriosa superba* plant leaf extract and their characterization studies have been reported for the first time.

G. superba L. belongs to Colchicaceae family. It is a perennial, greenish, climbing herb and native to South Africa. Its flower is a state flower of Tamil Nadu and national flower of Tamil Eelam [27]. Since 2000 B.C. it is being used as a traditional medicine by the tribes. Every part of the plant has been used in Siddha, Ayurveda and Unani system of medicine. *G. superba* is a tuberous plant with L- (or) V-shaped cylindrical tubers. The tuber powder has been effectively used against paralysis, rheumatism, snake bite, insect bites, against lice, intermittent fevers, wounds, anti-fertility, gonorrhea, leprosy, piles, debility, dyspepsia, flatulence, hemorrhoids, helminthiasis and inflammations [28]. It contains two major alkaloids namely colchicines and colchicosides. The seeds consist of colchicines, which are 2–5 times higher than in the tubers. Its leaf extract contains superbine, colchicine, gloriosine, gloriosol, phytosterils and stigmasterin [29].

In the present investigation, CeO_2 NPs are synthesized by using *G. superba* leaf extract. We have studied the structural, optical and antibacterial properties of CeO_2 NPs. To the best of our knowledge, this is the first report on the phytosynthesis of CeO_2 NPs by using *G. superba* leaf extract and their characterization studies such as

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Table. 1
Synthesis of CeO_2 nanoparticles by different methods.

S. no	Reference article	Description	Number of steps involved in the process	Total processing time
1	B. Choughury and A. Choudhury [14]	Hydrolysis	Single step	5 h
2	C. Hu et al. [15]	Composite hydroxide mediated	Single step	120 h
3	Y. Huang et al. [16]	Water-in-oil-micro-emulsion	Two step	16 h
4	A. Krishan et al. [17]	Thermolysis	Single step	1 h
5	S. Maensiri et al. [18]	Egg white synthesis	Single step	12 h
6	S. Maensiri et al. [19]	Plant extract	Single step	12 h
7	S. Phoka et al. [20]	Polymer complex	Single step	3 h
8	S. Sathyamurthy [21]	Reverse micellar	Two step	1 h
9	R. Suresh et al. [22]	Precipitation	Single step	20 h
10	Y. Tao et al. [23]	Microwave	Single step	5 h

XRD, TEM, UV–visible, FT-IR, Micro-Raman, photoluminescence and antibacterial activity analyses.

2. Materials and methods

2.1. Collection of plant material

The *G. superba* leaves were collected from Endangered Medicinal Plants Conservation Centre, Science Campus, Alagappa University, Karaikudi, Tamil Nadu, India. Taxonomic identification was made by Dr. S. John Britto, The Rapinat Herbarium and Centre for Molecular Systematics, St. Joseph's College, Tiruchirappalli, Tamil Nadu, India. The voucher specimen was numbered (KG-001) and preserved in the Department of Nanoscience and Technology, Alagappa University Karaikudi.

2.2. Synthesis of CeO_2 NPs using G. superba leaf extract

The 10 g of finely cut leaves was added with 100 mL of double distilled water and boiled at 50–60 °C for 5 min. The obtained extraction was filtered using Whatman No. 1 filter paper and the filtrate was collected in 250 mL Erlenmeyer flask and stored at room temperature for further usage. Thereafter, 3.72 g $CeCl_3$ salt was added to 100 mL of *G. superba* leaf extract. This solution was stirred constantly at a temperature of 80 °C for 4–6 h. A white precipitate formed and then it became a yellowish brown in color on continuous stirring. Further the precipitate was calcined at 400 °C for 2 h. Thus, CeO_2 nanopowder was obtained. A schematic diagram for the formation of CeO_2 NPs using *G. superba* leaf extract is shown in Fig. 1.

2.3. Characterization of CeO_2 NPs

The phytosynthesized CeO_2 NP samples were subjected to XRD analysis. The XRD pattern was recorded using Cu Kα radiation (λ = 1.54060 Å) with nickel monochromator in the range of 2θ from 10° to 80°. The average crystallite size of the synthesized CeO_2 NPs was calculated using Scherrer's formula [$D = 0.9\lambda/\beta\cos\theta$]. The XPS measurements were performed with XPS instrument (Carl Zeiss) equipment. The spectra were at a pressure using ultra high vacuum with Al Kα excitation at 250 W. The morphology of the synthesized CeO_2 was examined using TEM. Samples for TEM analysis were prepared by drop coating the nanoparticle solutions on carbon-coated copper grids at room temperature. The excess nanoparticle solution was removed with filter paper. The copper grid was finally dried at room temperature and was subjected to TEM analysis by the instrument Tecnai F20 model operated at an accelerating voltage of 200 kV. Moreover, Fourier transform infra-red spectroscopy (FT-IR) analysis was carried out in the range of 400–4000 cm^{-1} (PerkinElmer). The Micro-Raman analysis of our samples was carried out using the instrument of Princeton Acton SP2500, CS spectrometer 0.5 Focal length triple grating monochromator excitation source Ar^+ laser, 514.5 nm wavelength. UV–visible spectroscopy in the range of 200–850 nm used as Shimadzu spectrophotometer

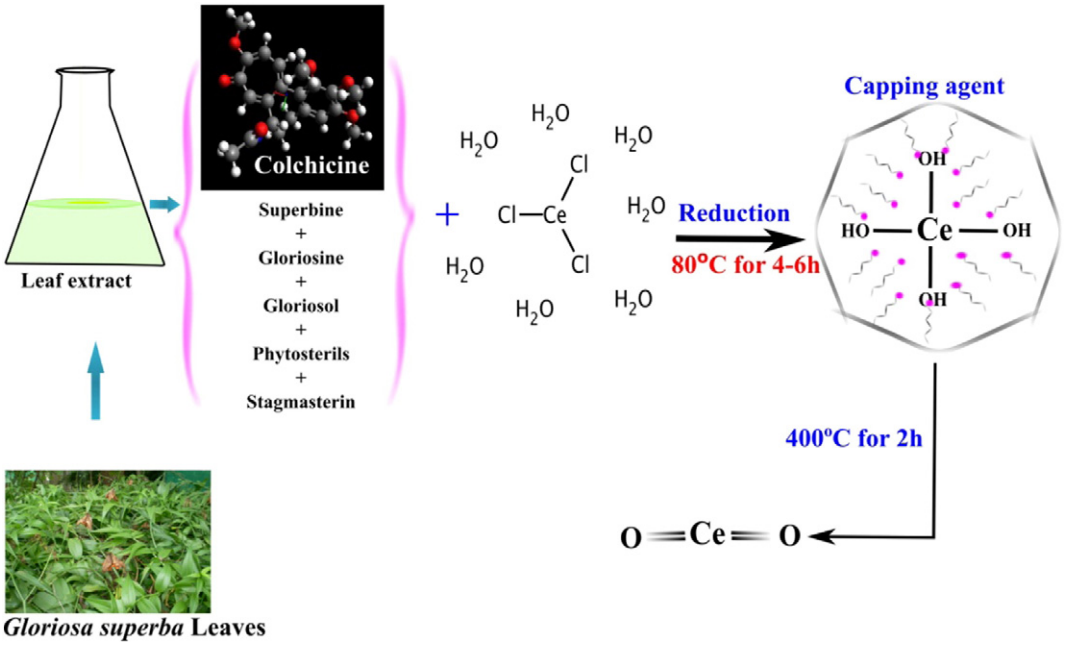

Fig. 1. Formation of CeO_2 NPs using *G. superba* leaf extract.